



[Exhibit A-1]

An invention relating to a "semiconductor integrated circuit device and method for manufacturing the same" is disclosed in Japanese Patent Application Kokai No. HEI 9-219501 (Exhibit A-1), which was laid open on August 19, 1997, a date prior to the filing of the present patent application. The following description is found in Figure 17 and [paragraph] [0053] of this [laid-open application]:

"Thus, in the present working configuration, when the upper electrode 28 is formed by depositing a TiN film 27 by means of a CVD process on top of the tantalum oxide film 24 that forms the capacitance insulating film 25 of the capacitance element used for information storage, an amorphous Ti film 26 that is impermeable to a nitrogen-containing reducing gas is formed beforehand on the surface of the tantalum oxide film 24, so that a deterioration in the withstand voltage (increase in the leak current) of the tantalum oxide film 24 can be securely prevented; accordingly, a DRAM with improved refresh characteristics can be realized."

Furthermore, the following description is found in Figures 35, 36, 37 and 39, and in [paragraphs] [0087] through [0089]:

"Next, a conductive film used for the upper electrode is deposited on top of the tantalum oxide film 77 using the CVD apparatus used in the aforementioned Working Configuration 1. The titanium-containing source gas used in this case is TiCl₄, TDMAT or TDEAT; the nitrogen-containing reducing gas is NH₃, MMH or a mixed gas consisting of these gases; and the inert gas is He, Ar, N₂ or a mixed gas consisting of these gases.

In the present working configuration, the gases are introduced into the chamber of the CVD apparatus according to the steps shown in Figure 35. Specifically, after the interior of the chamber has been evacuated to a specified degree of vacuum, the inert gas is introduced while the temperature of the substrate is elevated, and when the substrate temperature reaches a more or less constant value ... then, the nitrogen-containing reducing gas is introduced into the chamber and reacted with the titanium-containing source gas, so that a TiN film 79 is deposited on the surface of the protective film 78 as shown in Figure 37. Figure 38 shows the equation of a typical reaction between the titanium-containing source gas and the nitrogen-containing reducing gas.

...if this is done, then a protective film 78 is formed on the surface of the tantalum oxide film 77 by pyrolysis of the titanium-containing source gas, and this prevents contact between the tantalum oxide film 77 and the nitrogen-containing reducing gas that is introduced later, so that deterioration of the tantalum oxide film 77 is prevented."

[Furthermore,] the following description is found in Figures 41 and 42, and in [paragraphs] [0091] and [0092]:

"The optimal values of the film formation temperatures of the protective film 78 and TiN film 79 vary according to the type of titanium-containing source gas and nitrogen-containing reducing gas used and according to the combination of these gases that is

used; generally, however, in cases where NH_3 is used as the nitrogen-containing reducing gas, these temperatures are 550°C or less, and preferably 500°C or less. In cases where MMH is used, these temperatures are 500°C or less, and preferably 450°C or less.

Figures 41 and 42 are graphs which show the experimental results that were obtained when the relationship between the film formation temperatures of the above-mentioned protective film 78 and TiN film 79 and the electric field strength of the tantalum oxide film 77 was investigated. Figure 41 shows the electric field strength at 10^{-8} A/cm^2 in a case where a positive (+) voltage was applied to the upper electrode formed by the TiN film 79, while Figure 42 shows the electric field strength at 10^{-8} A/cm^2 in a case where a negative (-) voltage was applied to the above-mentioned upper electrode. The white circles (○) in the figures indicate a case in which film formation was accomplished by the steps shown in the aforementioned Figure 35 (inert gas = He + Ar, titanium-containing source gas = TiCl_4 , nitrogen-containing reducing gas = NH_3); the black circles (●) indicate a case in which film formation was accomplished by the steps shown in the aforementioned Figure 39 (inert gas = He + Ar, titanium-containing source gas = TiCl_4 , nitrogen-containing reducing gas = NH_3); the white squares (□) indicate a case in which film formation was accomplished by the steps shown in the aforementioned Figure 40 (inert gas = He + Ar, titanium-containing source gas = TiCl_4 , nitrogen-containing reducing gas = NH_3); and the black squares (■) indicate a case in which film formation was accomplished by the steps shown in the same Figure 40 (inert gas = He + Ar, titanium-containing source gas = TiCl_4 , nitrogen-containing reducing gas = NH_3 + MMH)."

Thus, an invention is disclosed which has substantially all of the specified items of the invention of the present patent, and which has an operation and effect similar to those of the invention of the present patent.

[Exhibit A-2]

An invention relating to a "CVD-TiN film formation method and semiconductor device manufacturing method" is disclosed in Japanese Patent Application Kokai No. HEI 10-177971 (Exhibit A-2), which was laid open on June 30, 1998, a date prior to the filing of the present patent application. The following description is found in [paragraph] [0033] of this [laid-open patent application]:

"In order to form a TiN film by means of such an apparatus, a semiconductor wafer W is first placed inside the chamber 31. Then, while the wafer W is heated by means of the heater 35, [the chamber 31] is evacuated to a high-vacuum state by means of the vacuum pump 39. Next, N_2 gas and NH_3 gas are introduced into the chamber 31 at a specified flow rate ratio, e.g., N_2 gas : 50 ~ 500 SCCM, NH_3 gas : 200 to 400 SCCM, so that the interior of the chamber 31 is [adjusted to a pressure of] (for example) 1 to 10 Torr, and pre-annealing is performed. Next, the interior of the chamber 31 is [adjusted to a

pressure of] 0.1 to 1 Torr, and TiCl₄ is introduced as a pre-flow for approximately 5 to 20 seconds at a flow rate of (e.g.) 5 ~ 20 SCCM, with the flow rates of the N₂ gas and NH₃ gas maintained "as is." Then, TiN film formation is performed for a specified time under the same conditions. Furthermore, it is desirable that a specified amount of (e.g.) N₂ gas be caused to flow as a purge gas during the period extending from the loading of the semiconductor wafer W into the chamber 31 to the completion of film formation. Alternatively, NH₃ gas and MMH gas may be used in combination."

Thus, items corresponding to the items described in [paragraph] [0018] of the gazette of the present patent are disclosed.